V. Conclusions and Recommendations for Further Work

In reference to the name of this project—Accelerated Removal and Validation—what we accomplished is best characterized as emphasizing *remediation* over *validation*. Our primary goal was to take advantage of the infrastructure and site conditions existant at TFF after the DUSDP to remove as much gasoline as we could with 24-h operations over a few months. In that context, we were quite successful. The estimated 1,000 gal of gasoline removed, which exceeds the amount estimated to be remaining in the areas not effectively cleaned by the DUSDP (about 750 gal, Newmark *et al.*, 1994), is about the same as that removed during the previous 3 months in which contaminant levels were steadily decreasing.

The strategy we used for advanced remediation during the ARV phase was driven by the time constraints that came with the funding for this work. This strategy, with limited time for lowering the water table, carrying out vapor extraction with different well configurations, air sparging, and renewed electrical heating, made it very difficult to assess the relative impact of each set of activities on the relative rate of contaminant removal. For example, we drew down water levels in the center of the TFF site and exposed the clay aquitard more effectively to vapor extraction, but because we were simultaneously carrying out vapor extraction, it is impossible to know how much effect this had on the ultimate recovery of hydrocarbons. It was not possible to have a control case in which we extracted vapor without drawing down the water table to use for comparison.

When operations were resumed in mid-January 1994, contaminant levels in the vapor and water phases were lower than any measured at the extraction wells at TFF. However, these levels may be misleading. The water table had been allowed to return to its pre-ARV phase levels. Thus, the clay aquitard and some of the upper part of the lower steam zone were no longer exposed to vapor extraction. For this reason alone, we would expect that concentrations in the vapor being recovered now would be lower. In addition, we removed and treated about one pore-volume of water from a very large area under the TFF site. This volume of water was replaced with relatively clean water, coming mainly from the south (Fig. 9). Some of this water may contain hydrocarbons driven outward from the site during the DUSDP, but these amounts are estimated to be relatively low (see Newmark *et al.*, 1994). It will take some time for aqueous concentrations to rise again, with sources remaining in small spatially localized areas.

The design of the electrodes in the newer heating wells apparently played a major role in the failure of electrical heating to significantly heat the formation, and specifically, the target "cold spot" in the clay zone. Clearly, electrode design (i.e., length and location of the conductor with respect to conductive parts of the formation and well completion details) and the configuration of the heterogeneous geology play a very important role in the electrical heating process. At this point, we are not ready to make any claims about the ability of electrical heating to enhance recovery of VOCs at the TFF site.

In the following paragraphs, we propose several activities that can be carried out during further activities at the TFF site that will help us (1) evaluate the location and significance of any remaining contamination in the cold spot, (2) assess the effect of lowering the water table on

removal by vapor extraction, (3) further validate our modeling of electrical heating, (4) develop a strategy to successfully heat the formation with electrical heating and assess its impact on the site, and (5) assess the ability of *in situ* bioremediation, perhaps enhanced with air sparging, to "polish" up the remaining clean-up activities.

The assessment of the location of the cold spot was done using preliminary assessments of DUSDP activities and chemical sampling results from the characterization wells that were drilled at the end of the DUSDP (which corresponded to the start of ARV). Final assessments of the DUSDP are now being completed, and a new assessment of the location, volume, and extent of contamination (e.g., a mass inventory) of the cold spot can now be completed with more confidence. Once this has been done, we recommend that an additional characterization well or wells be drilled at a site chosen to maximize our post-ARV knowledge about the cold spot, assess the effects of the ARV phase, and be used as a new electrical heating well. The additional wells will provide knowledge of the mass inventory in the zone, which can be used to assess the effect of subsequent electrical heating.

We further propose to again lower the water table by 24-h pumping (which we will be able to do once we automate the pump-and-treat system) to maximum drawdown levels obtained during the ARV without vapor extraction, and then maintain this configuration for about 2 weeks. Then, commencing vapor extraction with the lowered water table and comparing the contaminant removal results with the steady-state prior to drawdown, we will be able to assess the effect of lowering the water level on THC removal rate. If the results show no difference, it will enhance our confidence that the site has indeed been cleaned to a significant degree.

We clearly need to validate the model of electrical heating. A variety of experiments using the existing equipment could be conducted. Several more model runs could confirm the highest payoff approach.

Additional studies of processes occurring around the heater electrodes are necessary to improve our understanding of the physics of the heating process and to validate our computer models. By applying current to sets of two electrodes at a time, such as two of the new long electrodes, two of the original short electrodes, and a combination of short and long electrodes, we can more closely match conditions of the computer simulation. During electrical heating, we will carefully monitor conditions in the borehole (temperature, current, vapor quantity, and composition) to try to discern what is happening in the near field. Once these field tests have been carried out and checked against the model simulations, the model can be adjusted accordingly to give us more confidence in its ability to predict what will happen for a given electrode configuration.

After completing the above work, we will be in a better position to design an electrode configuration to be put into the post-ARV characterization well or wells. Using the computer simulation, we will design the electrodes to be more compatible with the existing configuration (probably using only the original short electrodes), which will optimize our ability to heat the clay zone in the cold spot. We will also be able to simulate electrical heating in conjunction with vapor extraction and water table drawdown for better contaminant removal.

We have submitted a proposal for EM50 funding of a project to improve our knowledge of electrical heating and to develop improved computational tools for system design. The proposal

includes the design application to the TFF cold spot as well as smaller-scale designs for possible application at secondary areas of contamination in the TFF area not affected by the DUSDP.

The DUSDP was very successful in removing gasoline from the upper and lower steam zone aquifers and probably removed a significant amount of contamination from the intervening clay aquitard. ARV and the follow-up steps explained above should lead us to a condition at TFF where all remaining sources of significant contamination have been removed. What will remain is the "polishing" step of getting the site in compliance with the 1-ppb benzene clean water standard for California. With traditional pump-and-treat and vapor extraction, it will still take considerable time to reach 1 ppb of benzene. This process can be accelerated by the use of enhanced biodegradation. Studies are already going on at LLNL to identify and culture indigenous microbes that break down gasoline into more innocuous chemistry. Planning for a final polishing step using biodegradation is in progress and should be considered as a cost-effective means to reach final closure of the TFF site.

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List of Acronyms

ACWP	actual cost of work performed
ARV	Accelerated Removal and Validation
BAAQMD	Bay Area Air Quality Management District
BCWS	Budgeted Cost of Work Scheduled
BTEX	benzene, toluene, ethyl benzene, and total xylenes
CoC	Chain-of-Custody
CRS	Continental Recovery Systems
DUSDP	Dynamic Underground Stripping Demonstration Project
ELCD	electrolytic conductivity detector
EPA	U.S. Environmental Protection Agency
ERD	Environmental Restoration Division
ERT	electrical resistance tomography
ES&H	Environmental Safety and Health
GAC	granular activated carbon
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrometer
GSA	Gasoline Spill Area
HC	hydrocarbons
ICE	internal combustion engine
ISTD	internal standard
LDV	low dead volume injector
LLNL	Lawrence Livermore National Laboratory
LOD	limit of detection
LSZ	lower steam zone
mg/L	milligrams per liter
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NPDES	National Pollutant Discharge Elimination System
NUFT	Nonisothermal Unsaturated-Saturated Flow and Transport
OVA	organic vapor analyzer
OVM	organic vapor meter
OWS	oil/water separator

pH	puissance d'Hydrogène (hydrogen potential)
PID	photoionization detector
ppmv	parts per million by volume
Pvp	pressure and vapor pressure
QAP	Quality Assurance Plan
RSD%	Relative Standard Deviation Percent
SOP	Standard Operating Procedure
STP	Standard Temperature and Pressure
TFF	Treatment Facility F
TH	total hydrocarbons
TPH	total petroleum hydrocarbons
USZ	upper steam zone
VAC	volts AC (alternating current)
VOA	volatile organic analysis
VOC	volatile organic compound

Glossary

Accuracy -- Combination of bias and precision of an analytic procedure, which reflects the closeness of a measured value to a true value.

Bias -- Consistent deviation of measured values from the true value, caused by systematic errors in a procedure.

Calibration standard – A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The calibration standard solutions are used to calibrate the instrument response with respect to analyte concentration.

Calibration check standard – Standard used to determine the state of calibration of an instrument between periodic recalibrations.

Detection limit – The lowest concentration level that can be determined to be statistically different from a blank.

Duplicate – Usually, the smallest number of replicates (two), but here specifically refers to duplicate samples, i.e., two samples taken at the same time from one location.

Field duplicates – Two separate samples collected at the same time, placed under identical conditions, and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Field reagent blank – Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytic procedures. The purpose of the field reagent blank is to determine if method analytes or other interferences are present in the field environment.

Internal standard – A pure compound added to a solution in known amounts and used to measure the relative responses of other method compounds and surrogates that are components of the same solution.

Laboratory duplicates – Two sample aliquots taken in the analytic laboratory and analyzed separately with identical procedures. Analysis of laboratory duplicates gives a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

Laboratory-fortified blank – An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The laboratory-fortified blank is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

Laboratory-fortified sample matrix – An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The laboratory-fortified sample matrix is analyzed exactly like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytic results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot, and the measured values in the laboratory-fortified sample matrix must be corrected for background concentrations.

Laboratory performance check solution – A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

Laboratory reagent blank – An aliquot of reagent water that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The laboratory reagent blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

Method detection limit – The lowest concentration of analyte that a method can detect reliably in either a sample or blank.

Precision – Measure of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation.

Primary dilution standard solution – A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

Quality assessment – Procedure for determining the quality of laboratory measurements by use of data from internal and external quality control measures.

Quality assurance – A definitive plan for laboratory operation that specifies the measures used to produce data of known precision and bias.

Quality control sample – A sample matrix containing method analytes or a solution of method analytes in a water-miscible solvent that is used to fortify reagent water or environmental samples. The quality control sample is obtained from a source external to the laboratory and is used to check laboratory performance with externally prepared test materials.

Stock standard solution – A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

Surrogate standard – A pure standard, which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount just before processing so that the overall efficiency of a method can be determined.